(19) Japan Patent Office (JP)
(11) Japanese Patent Laid-Open Number: Hei 9-161666
(12) Publication of Unexamined Patent Applications (A)
(43) Laid-Open Date: Heisei 9-6-20 (June 20, 1997)
(51) Int. Cl.^{6} Identification Code Office Reference Number F1
H 01 J 9/02 H 01 J 9/02 B
1/30 1/30 A
Request for Examination: No request to be done
Number of Claims: 14 FD (fifteen pages in total)

(21) Application Number: Hei 7-347383
(22) Filed: Heisei 7-12-13 (December 13, 1995)

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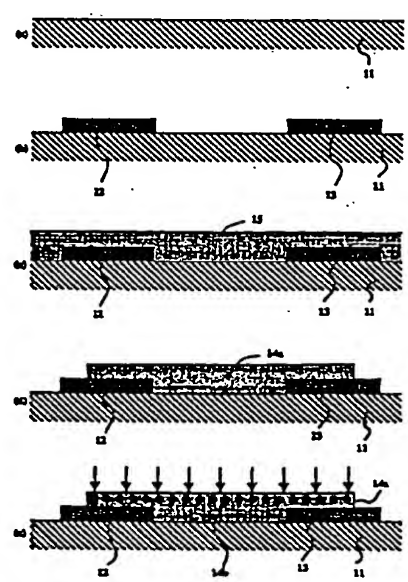
(54) [Title of the Invention] Manufacturing Method of Electron Emission Device

(57) [Abstract]
[Object of the Invention] To manufacture an electron emission device capable of emitting electrons stably with simple processes.
[Solving Means] A pair of electrodes 12 and 13 is formed on a glass substrate 11 (Fig. (b)). A resin layer 15 showing thermal plasticity is formed thereon (Fig. (c)), and is patterned. Thus, a resin layer 14a is formed (Fig. (d)). This substrate 11 is introduced into a chamber, and heated. The resin layer



14a is softened. When an electrically conductive material is heated and evaporated while keeping the chamber in a vacuum, fine particles 14b formed of the electrically conductive material are implanted into the resin layer 14a softened (Fig. (e)). In the above described manner, a thin film structure in which the electrically conductive fine particles 14b are uniformly dispersed in the resin layer 14a is obtained. The resin layer 14a functions as a high resistance layer, and when a voltage is applied between electrodes 12 and 13, electron emissions from a surface of the resin layer 14a are observed.

[What is claimed is]

[Claim 1] A method of manufacturing an electron emission device having an electron emission layer ,which is formed by allowing fine particles formed of an electrically conductive material to disperse in a high resistance layer formed of an electrically insulative material, comprising the steps of:

forming a resin layer having thermal plasticity on a substrate; and

implanting fine particles formed of an electrically conductive material from a surface of said resin layer in a state where said resin layer is softened by heating said resin layer, thus forming electron emission layer in which said fine particles are dispersed at a predetermined depth of said resin layer.

[Claim 2] The method of manufacturing an electron emission device according to claim 1, wherein the substrate having the resin layer formed thereon and the electrically conductive material are enclosed within a chamber, said resin layer is softened by heating said substrate while keeping the chamber in a predetermined vacuum, said electrically conductive material is evaporated by heating said electrically conductive material, and the fine particles formed of said electrically conductive material are implanted from the surface of said resin layer thereinto.

[Claim 3] The method of manufacturing an electron emission device according to claim 1, wherein a first chamber enclosing the electrically conductive material and a second chamber enclosing

the substrate having the resin layer formed thereon are prepared, a transfer pipe for transferring a gas in said first chamber to said second chamber is provided, and a gas is exhausted from said second chamber while introducing inert gas for said electrically conductive material into said first chamber, thus introducing a gas in said first chamber to said second chamber via said transfer pipe; and wherein said electrically conductive material is evaporated by heating said electrically conductive material in said first chamber so that the fine particles formed of said electrically conductive material are generated and introduced into said second chamber, and said resin layer is softened by heating said second substrate in said second chamber so that said fine particles are implanted from the surface of said resin layer thereinto.

[Claim 4] The method of manufacturing an electron emission device according to claim 3, wherein reactive gas having a nature to react with said electrically conductive material to generate an electrically insulative compound is made to react with surfaces of fine particles formed of the electrically conductive material, fine particles formed of the electrically conductive material, the surfaces of which are covered with said electrically insulative compound, are generated , and fine particles are implanted from the surface of the resin layer thereinto.

[Claim 5] The method of manufacturing an electron emission device according to any one of claims 1, 2, 3 and 4, wherein a plurality of sections are defined on the substrate, and a pair of electrodes is formed on each section ,reaspectively;

the independent resin layer contacting said pair of electrodes is formed on an individual specific area which is decided for each section on said substrate respectively;

fine particles are selectively implanted only to said specific area among all areas of said substrate; and

an independent electron emission device is formed for each section on said substrate,respectively.

[Claim 6] The method of manufacturing an electron emission device according to any one of claims 1, 2, 3 and 4, wherein a plural-

ity of sections are defined on the substrate, and a pair of electrodes is formed on each section respectively;

a wide area resin layer is formed on an area overpassing the plurality of sections on said substrate, and then the independent layer contacting said pair of electrodes is formed on the independent specific area defined for each section by patterning this wide area resin layer;

fine particles are selectively implanted only to said specific area among all areas of said substrate; and

an independent electron emission device is formed for each section on said substrate, respectively.

[Claim 7] The method of manufacturing an electron emission device according to any one of claims 1, 2, 3 and 4, wherein a plurality of sections are defined on the substrate, and a pair of electrodes is formed on each section respectively;

a wide area resin layer is formed on an area overpassing the plurality of sections on said substrate, and fine particles are selectively implanted only to an individual specific area decided for each of said sections among all areas of this wide area resin layer ; and

an independent electron emission device is formed for each section on said substrate respectively.

[Claim 8] The method of manufacturing an electron emission device according to claim 7, wherein, after fine particles are implanted, patterning for leaving each specific area among all areas of the wide area resin layer is performed, and an independent resin layer is formed on the individual specific area respectively.

[Claim 9] The method of manufacturing an electron emission device according to any one of claims 1, 2, 3 and 4,

wherein a plurality of sections is defined on the substrate, and a pair of electrodes is formed on each section respectively;

a wide area resin layer is formed on an area overpassing the plurality of sections on said substrate, and fine particles are implanted to all areas of this wide area resin layer;

patterning is subsequently performed so as to leave an in-

dividual specific area decided for said each section in said wide area resin layer, and an independent resin layer contacting said pair of electrodes is formed in the individual specific area respectively.

[Claim 10] The method of manufacturing an electron emission device according to any one of claims 6, 8 and 9,

wherein the wide area resin layer is formed by resin having photosensitivity, and patterning is performed by exposure for this photosensitive wide area resin layer.

[Claim 11] The method of manufacturing an electron emission device according to any one of claims 5, 6, 7 and 8,

wherein a shielding mask having an opening window corresponding to the specific area of the each section is arranged for the substrate, and fine particles are selectively implanted only into this opening window.

[Claim 12] The method of manufacturing an electron emission device according to any one of claims 5, 6, 7 and 8,

wherein the fine particles are allowed to emit from a nozzle at a speed suitable for implantation to the resin layer;

providing opening/closing means for opening/closing said nozzle and scanning means for scanning a position of the nozzle for a substrate plate; and

controlling emission/non-emission of the fine particles by said opening/closing means and scanning the nozzle by said scanning means, thus selectively implanting the fine particles only to each specific area.

[Claim 13] The method of manufacturing an electron emission device according to any one of claims 1 to 12,

wherein after the implantation of the fine particles, a forming treatment to cause a change of properties by Joule heat by energizing the resin layer.

[Claim 14] The method of manufacturing an electron emission device according to any one of claims 1 to 12,

wherein the resin layer is formed by resin having an electrical polarity, after the fine particles are implanted, said resin

layer is softened by heating said resin layer while applying electrical field at a predetermined direction, and a pauling treatment for polymerizing said resin layer is performed in a state where resin is oriented in a predetermined direction.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] The present invention relates to a method of manufacturing an electron emission device, more particularly to a method of manufacturing an electron emission device having an electron emission layer formed by allowing fine particles formed of an electrically conductive material to disperse in a high resistance layer formed of an electrically insulative material.

[0002]

[Prior Arts] As one kind of flat panel displays, a FED (Field Emission Display) has been eagerly studied. In this FED, a cathode substrate and an anode substrate are made to face each other, and a large number of electron emission devices are arranged on the cathode substrate. Each of the electron emission devices is caused to emit electrons toward the anode substrate therefrom, and a fluorescent layer on the anode substrate is caused to emit light. The electron emission device formed on the cathode substrate corresponds to each pixel. The electron emission device that has been heretofore used has generally an acute structure suitable for electron emission, and for example the electron emission device formed of a conical metal having an acute tip portion has been widely used.

[0003] As opposed to this, a surface conduction type electron emission device recently has drawn attention. This surface conduction type electron emission device is the one utilizing phenomenon in which electron emission occurs by allowing current to flow in parallel with a plane of a thin film of a small area, formed on a substrate. Various reports have been made for such electron emission phenomenon ever since this phenomenon has been reported by M. I. Elison et al. in "Radio Eng. Eletctron. Phys.", Vol. 10, pp. 1290 to 1296, 1965. To be more specific, these reports were made as to a

Au thin film, an ITO thin film, a carbon thin film in addition to a SnO2 (Sb) thin film, developed by M. I. Elison et al., and the surface conduction type electron emission phenomenon was reported. Such phenomenon has been known to be a peculiar electron emission phenomenon occurring in a thin film where a high resistance area locally exists. A forming treatment for forming the local high resistance area is usually carried out. For example, Japanese Examined Patent Publication No. Hei 6(1994)-87392 shows a method of manufacturing an electron emission device having an surface conductive type electron emission function, by electrifying a electrically conductive thin film containing fine particles so as to heat this thin film. In this method, by the forming treatment in which energizing/heating is performed, a fissure can be caused locally in the electrically conductive thin film, and the fissure region function as a high resistance area.

[0004]

[Subjects to be Solved by the Invention] However, in the method of manufacturing in which the above described forming treatment is carried out, it is very difficult to manufacture a device capable of stably emitting electrons. When an electrically conductive thin film is formed on a substrate and the forming treatment such as energizing/heating is carried out for this electrically conductive thin film, a fissure occur locally in the thin film by the energizing/breaking, and the fissure region function as a high resistance area. Accordingly, to realize stable election emission, the fissure need to be generated uniformly in the thin film. However, in this forming treatment step, it is difficult to control generation spot of the fissure and size thereof. To realize a device capable of emitting electrons stably, a high level technique is necessary for this forming treatment step.

[0005] Moreover, as described above, the surface conduction type electron emission device is the one which is expected to be used for a flat panel display such as FED. When the surface conduction type electron emission device is applied to such display, a large number of devices are arranged on a substrate in a matrix fashion,

and it is necessary to obtain stable and uniform electron emission from each device. If devices performing an unstable operation exist in mixed way, unevenness occurs in displaying of a screen as a display, and it is no longer impossible to realize a high quality display. For this reason, a characteristic of the individual electron emission device constituting each pixel need to be made to be as uniform as it can be, and stable electron emission need to be obtained from all devices. Accordingly, in the case of the electron emission device used for a display, a higher level forming treatment is required.

[0006] To solve such problems of such forming treatment, in Japanese Examined Patent Application Hei 6(1994)-101297, a structure of an electron emission device which doesn't require the forming treatment has been proposed. Specifically, in this gazette, a technology is disclosed, in which fine particles are dispersed on a surface of a first electrically insulating layer, and a second electrically insulating layer is formed on the first electrically insulating layer, thus forming a structure in which the dispersed surface of the fine particles is sandwiched by the electrically insulating layers, so as to constitute a surface conduction type electron emission device. However, this structure requires sandwiching the dispersed surface of the fine particles by the insulating layers, so that a new problem of complexity of manufacturing processes is created.

[0007] So the object of the present invention is to provide a manufacturing method capable of manufacturing an electron emission device, which can emit electron stably, with simple steps.

[0008]

[Means for Solving Subjects]

(1) The first aspect of the present invention of a method of manufacturing an electron emission device having an electron emission layer which is formed by allowing fine particles formed of an electrically conductive material to disperse in a high resistance layer formed of an electrically insulative material, the method comprising the steps of: forming a resin layer having thermal plasticity on

a substrate; and implanting fine particles formed of an electrically conductive material from a surface of the resin layer in a state where the resin layer is softened by heating the resin layer, thus forming an electron emission layer in which the fine particles are dispersed at a predetermined depth of the resin layer.

[0009] (2) The second aspect of the present invention of the method of manufacturing an electron emission device according to the first aspect, wherein the substrate having the resin layer formed thereon and the electrically conductive material are enclosed within a chamber, the resin layer is softened by heating the substrate while keeping this chamber in a vacuum, the electrically conductive material is evaporated by heating the electrically conductive material, and the fine particles formed of the electrically conductive material are implanted from the surface of the resin layer thereinto.

[0010] (3) The third aspect of the present invention of the method of manufacturing an electron emission device according to the first aspect, wherein a first chamber enclosing the electrically conductive material and a second chamber enclosing the substrate having the resin layer formed thereon are prepared, a transfer pipe for transferring a gas in the first chamber to the second chamber is provided, and a gas is exhausted from the second chamber while introducing inert gas for the electrically conductive material into the first chamber, thus introducing a gas in the first chamber to the second chamber via the transfer pipe; and wherein the electrically conductive material is evaporate by heating said electrically conductive material in the first chamber so that the fine particles formed of the electrically conductive material are generated and these fine particules are introduced into the second chamber, and the substrate is softened by heating the substrate in the second chamber so that the fine particles are implanted from the surface of the resin layer thereinto.

[0011] (4) The fourth aspect of the present invention of the method of manufacturing an electron emission device according to the third aspect, wherein reactive gas having a nature to react with

this electrically conductive material to generate an electrically insulative compound is made to react with surfaces of fine particles formed of the electrically conductive material, fine particles formed of the electrically conductive material, the surfaces of which are covered with the electrically insulative compound, are generated , and these fine particles are implanted from the surface of the resin layer thereinto.

[0012] (5) The fifth aspect of the present invention of the method of manufacturing an electron emission device according to the first to fourth aspects, wherein a plurality of sections are defined on the substrate, and a pair of electrodes is formed on each section respectively; the independent resin layer contacting the pair of electrodes is formed on an individual specific area which is decided for each section on the substrate respectively; fine particles are selectively implanted only to the individual specific area among all areas of the substrate; and an independent electron emission device is formed for each section on the substrate respectively.

[0013] (6) The sixth aspect of the present invention of the method of manufacturing an electron emission device according to the first to fourth aspects, wherein a plurality of sections are defined on the substrate, and a pair of electrodes is formed on each section respectively; a wide area resin layer is formed on an area overpassing the plurality of sections on the substrate, and then the independent resin layer contacting the pair of electrodes is formed on the independent specific area defined for each section by patterning this wide area resin layer ,respsctively; fine particles are selectively implanted only to the specific area among all areas on the substrate respectively; and an independent electron emission device is formed for each section of the substrate.

[0014] (7) The seventh aspect of the present invention of the method of manufacturing an electron emission device according to the first to fourth aspects, wherein a plurality of sections are defined on the substrate, and a pair of electrodes are formed on each section respectively; a wide area resin layer is formed on an area overpassing the plurality of sections on the substrate, and fine

particles are selectively implanted only to an individual specific area decided for each of the sections among all areas of this wide area resin layer; and an independent electron emission device is formed for each section on the substrate respectively.

[0015] (8) The eighth aspect of the present invention of the method of manufacturing an electron emission device according to the seventh aspect, wherein, after fine particles are implanted, patterning for leaving each specific area only among all areas of the wide area resin layer is performed, and an independent resin layer is formed on the individual specific area respectively.

[0016] (9) The ninth aspect of the present invention of the method of manufacturing an electron emission device according to the first to fourth aspects, wherein a plurality of sections are defined on the substrate, and a pair of electrodes is formed on each section respectively;

a wide area resin layer is formed on an area overpassing the plurality of sections on the substrate, and fine particles are implanted to all areas of this wide area resin layer; patterning is subsequently performed so as to leave an individual specific area decided for each section in the wide area resin layer, and an independent resin layer contacting the pair of electrodes is formed in the individual specific area respectively.

[0017] (10) The tenth aspect of the present invention of the method of manufacturing an electron emission device according to the sixth, eighth and ninth, wherein the wide area resin layer is formed by resin having photosensitivity, and patterning is performed by exposure for this photosensitive wide area resin layer.

[0018] (11) The eleventh aspect of the present invention of the method of manufacturing an electron emission device according to the fifth to eighth aspects, wherein a shielding mask having an opening window corresponding to the specific area of the each section is arranged for the substrate, and fine particles are selectively implanted only into the opening window.

[0019] (12) The twelfth aspect of the present invention of the method of manufacturing an electron emission device according to

the fifth to eighth aspects, wherein the fine particles are allowed to emit from a nozzle at a speed suitable for implantation to the resin layer; providing opening/closing means for opening/closing the nozzle and scanning means for scanning a position of the nozzle for a substrate plane; and controlling emission/non-emission of the fine particles by the opening/closing means and scanning the nozzle by the scanning means, thus selectively implanting the fine particles only to each specific area.

[0020] (13) The thirteenth aspect of the present invention of the method of manufacturing an electron emission device according to the first to twelfth aspects, wherein after the implantation of the fine particles, a forming treatment to cause a change of properties by Joule heat by energizing the resin layer is performed.

[0021] (14) The fourteenth aspect of the present invention of the method of manufacturing an electron emission device according to the first to twelfth aspects, wherein the resin layer is formed by resin having an electrical polarity, and after the implantation of the fine particles are implanted, the resin layer is softened by heating the resin layer while applying electrical field in a predetermined direction, and a pauling treatment for polymerizing the resin layer is performed in a state where resin is oriented in a predetermined direction.

[0022]

[Embodiments] The present invention will be described based on embodiments illustrated below.

[0023] § 1. A structure of the conventional electron emission device and an operation thereof

A structure of the conventional general surface conduction type electron emission device and its operation are first described. Fig. 1 is a section view showing structures of the conventional surface conduction type electron emission device 10 and an opposite substrate 20. In this example, the electron emission device 10 is constituted by forming electrodes 12 and 13 on a glass substrate 11 and by forming an electron emission layer 14 thereon. The electron emission layer 14 functions as a cathode electrode, and may

be constituted of any material as long as it is known to exhibit surface conduction type electron emission phenomenon, such as metal oxides including SnO_2, In_2O_3 and PbO, a metal including Au and Ag and various kinds of semiconductors including carbon. On the other hand, the opposite substrate 20 is constituted by forming a transparent electrode 22 and a phosphor layer 23 on the glass substrate 21. For example the transparent electrode 22 is constituted of a material such as ITO and functions as an anode electrode.

[0024] Fig. 2 is a top plan view of constituent components formed on the glass substrate 11 in the electron emission device shown in Fig. 1. The section view taken along the line I-I in this figure is shown in Fig. 1. Clearly shown is a situation in which the electrodes 12 and 13 face each other with a predetermined gap, and the electron emission layer 14 is formed between them.

[0025] Consideration will be now given to the phenomenon caused when a wiring is performed in each portion as shown in Fig. 1. By wiring, the electrode 13 is grounded, and a negative voltage is applied to the electrode 12 from a power source 31. Furthermore, an inter cathode and anode voltage is applied between the electron emission device 10 and the opposite substrate20 by the power source 32,however a switch 33 is made to be open in the state shown in Fig. 1. Accordingly, an application of a voltage is not being performed. When a voltage is applied to both sides of the electron emission layer 14 by the electrodes 12 and 13, electron emissions occur at the surface portion of the film of the electron emission layer 14 as shown by arrows in Fig. 1. This is phenomenon that is known as the surface conduction type electron emission.

[0026] When the inter cathode and anode voltage is applied by closing the switch 33, electrons emitted in the surface of the electron emission layer 14 fly to the opposite substrate 20 on the anode side as shown in Fig. 3, and electrons traveling from the cathode to the anode collide against the phosphor layer 23. Thus, the phosphor layer 23 emits fluorescence. For convenience of the descriptions, the constituent components of one pixel are here

shown. If such constituent components of for one pixel are arranged vertically and horizontally in a matrix fashion, a flat panel display in which the pixels are arranged on a two-dimensional plane can be obtained. By the way, in such flat display panel, a voltage applied from the power source 31 to each pixel is controlled in a state where the switch 33 is kept close, and a light emission state for each pixel is generally controlled. To be more specific, by controlling a value of the voltage applied to the electron emission layer 14 and an application time, a quantity of flies of the electrons to the opposite substrate 20 side can be controlled.
[0027]To form the electron emission layer having such electron emission characteristic, a forming treatment for the electrically conductive thin film has heretofore been performed. Specifically, as shown in a sectional side view of Fig. 4, after the pair of electrodes 12 and 13 is formed on the glass substrate 11, the electrically conductive thin film 14Z is formed, and a current If for forming, which is comparatively large, is supplied between the electrodes 12 and 13 from the power source 34. The electrically conductive thin film 14z is locally broken down, deformed and degenerated by Joule heat, and electrically high resistance area (Specifically, fissure having a size of about 0.5 μm to 5 μm) are generated and the formation of the electron emission layer 14 has been performed. However, in such forming step, since it is impossible to control precisely the spot where the fissure is caused and the size of the fissure, it is difficult to form the electron emission layer 14 capable of stably emitting electrons, as described above.
[0028] <u>§2. A structure of an electron emission device of the present invention and its operation</u>
Although the present invention relates to a method of manufacturing an electron emission device, for convenience of descriptions, a structure of an electron emission device manufactured by a method according to the present invention and its operation will be described. The electron emission device according to the present invention is a surface conduction type electron emission device as shown in Fig. 1, in which the electron emission layer 14 is consti-

tuted of a layer obtained by dispersing fine particles formed of a electrically conductive material in a high resistance layer formed of an electrically insulative material. Fig. 5 is an enlarged section view for explaining a basic structure of the electron emission layer 14, and shows a state where the fine particles 14b formed of the electrically conductive material are dispersed in the high resistance layer 14a formed of the electrically insulative material. Generally, the word "ultra fine particles" is used for fine particles having a diameter of 100 nm or less. In this embodiment, ultra fine particles having sizes of an average diameter of about 100 nm are used as the fine particles 14b. Furthermore, in this embodiment, the maximum thickness of the high resistance layer 14a formed of the electrically insulative material, that is, a thickness of a central portion of Fig. 5 , is about 300 nm, each of the fine particles 14b is buried at a position which is about 40 nm deep from the surface of this layer. Although the position from the surface of the layer somewhat varies for each of the fine particles 14b, any of the fine particles 14b is buried in an almost equal position with respect to the depth, and a state where a large number of fine particles 14b are uniformly dispersed two-dimensionally in a plane in parallel with the substrate is obtained.

[0029] As described above, when the electron emission layer 14, which is obtained by dispersing the fine particles 14b formed of the electrically conductive material in the high resistance layer 14a formed of the electrically insulative material, is formed on the substrate 11, the electron emission phenomenon is caused from this electron emission layer 14. Specifically, in the structural body shown in Fig. 5, when a predetermined application voltage V1 is applied between both electrodes 12 and 13, current flows through a large number of fine particles 14b dispersed, and the electron emission phenomenon is observed from the surface of the electron emission layer 14. Such phenomenon is observed when diameters of the fine particles 14b and a dispersion density are kept in predetermined conditions. Specifically, as shown in Fig. 6, when a diameter of the fine particles 14b in the high resistance

layer 14a is set to D1 and a gap between one fine particle and other fine particle closest to one fine particle is set to D2, when D1 and D2 adopt values of a predetermined range, such electron emission phenomenon occurs. According to experiments performed by the inventors of the present invention, the upper limit value of the particle diameter D1 is assumed to be about 100 nm. When electrically conductive fine particles of a diameter D1 equal to 100 nm or less are used, the present invention can be realized. On the other hand, since conditions relating to the gap D2 between one particle and other particles adjacent to one particle depend on a diameter of the particle and a shape thereof, it is generally impossible to determine a numerical value condition. However, it is an indisputable fact that a certain degree of a numerical value range exists. Specifically, if the gap D2 becomes too small, the whole of the electron emission layer 14 functions as a mere electrically conductive layer, and the electron emission phenomenon comes not to be caused. Contrary to this, if the gap D2 becomes to large, the electron movement between the fine particles doesn't come to occur, and the whole of the electron emission layer 14 functions as a mere electrically insulative layer. After all, the electron emission phenomenon doesn't come to be caused. Although determination of the gap D2 for causing the electron emission phenomenon or a critical condition concerning a particle distribution density is not made at this time, effective electron emission can be overall achieved according to the experiment with setting D1 to approximately equal to D2. In this embodiment, D1 and D2 are set to about 20 nm. It should be noted that according to the manufacturing method of the present invention which will be described later , it is possible to control the diameter of the electrically conductive fine particles 14b and the dispersion density thereof freely.

[0030] In such structural body, a close-up theoretical speculation about the reason why the electron emission phenomenon occurs is not performed at this stage. However the inventors of the present invention consider that environment to cause the electron emission to be apt to occur is given rise to for the following reason in a

state the electrically conductive ultra fine particles of a diameter equal to 100 nm or less are dispersed in the high resistance layer in the above described manner. Specifically, electric discharge phenomenon such as corona discharge is generally known to occur from an acute tip end. It is not difficult to imagine that the electrically conductive ultra fine particles of a diameter equal to 100 nm or less will perform a function identical to that of this acute tip end. Accordingly, the electron emission can be considered to occur similarly to the electric discharge from a tip of a needle in a vacuum, when such fine electrically conductive ultra fine particles are dispersed in the high resistance layer. Particularly, in Fig. 5, assuming that a negative voltage is applied to the electrode 12 side, excessive charges are considered to be generated due to the application of the negative voltage at a region in the vicinity of the electrode 12 of the electron emission layer 14, and these excessive charges are supposed to contribute to the electron emission. Note that , according to the manufacturing method of the present invention, which will be described later, since a state where the electrically conductive ultra fine particles are dispersed in the high resistance layer as shown in Fig. 5 can be obtained at once, it is unnecessary to cause minute fissure in the layer like the conventional way, and the forming treatment that was required conventionally is not always necessary.

[0031] According to the electron emission device having the above-described structure, very stable electron emission is obtained from the surface of the electron emission layer 14. The electron emission layer 14 is a layer obtained by dispersing the electrically conductive fine particles 14b in the high resistance layer 14a, as shown in Fig. 5. As a matter of course, when viewing individual fine particles in terms of micro-size, the diameter D1 and the shape are different among the respective fine particles, and the gap D2 between one fine particle and other fine particles adjacent to one fine particle differs. However, when the whole of the electron emission layer 14 is observed in terms of macro-size, the diameters of each ultra fine particle and the distribution state can

be presumed to be even, and very stable electron emission can be achieved. Moreover, when a display device displaying one pixel by means of this single electron emission layer 14 is manufactured, a large number of independent electron emission layers 14 are formed on the supporting substrate. However, when viewing the display device in terms of macro-size, the particle diameter of the ultra fine particles in each electron emission layer 14 and the distribution state thereof are substantially even, display characteristics among the pixels are also even. For this reason, the display device with a high quality free from unevenness of the display characteristic among the pixels can be realized.

[0032] § 2. A structure of another electron emission device to which the present invention is to be applied

The manufacturing method according to the present invention is not limited only to the electron emission device having the structure shown in Fig. 1, but, in addition to this electron emission device, applicable to the case where electron emission devices having various kinds of structures are manufactured. The manufacturing method according to the present invention is widely applicable to the electron emission device having the structure that the electron emission layer obtained by dispersing the fine particles formed of the electrically conductive material as well as the pair of electrodes which contacts this electron emission layer and is disposed with a predetermined gap between each of them is formed. Several structures of the electron emission device to which the present invention is applicable are exemplified below.

[0033] In the structure shown in Fig. 1 or Fig. 5, the electrode 12, the electron emission layer 14 and the electrode 13 are arranged on the supporting substrate 11 laterally. Contrary to this, in the structure shown in Fig. 7, these are arranged vertically. Specifically, as shown in Fig. 7(a), a three-layered structural body in which the lower electrode layer 52, the middle insulative layer 53 and the upper electrode layer 54 are laminated is formed on the supporting substrate 51 (not shown), and the electron emission layer 55 is further formed on the side and end portion of the three-

layered structural body as shown in Fig. 7(b). Here, the electron emission layer 55 is a thin film layer obtained by dispersing electrically conductive fine particles in a high resistance layer like the example shown in Fig. 5. Also by such structure, the electron emission device 50 can be formed.

[0034] Specifically, as shown in the side sectional view of Fig. 8, the three-layered structural body in which the lower electrode layer 52, the middle insulative layer 53 and the upper electrode layer 54 are laminated is formed on the glass substrate 51, and the electron emission device 50 having the electron emission layer 55 is further prepared on the side and end portion of the three-layered structural body. Then, the opposite substrate 20 is disposed above the three-layered structural body. The opposite substrate 20 is constituted by forming the transparent electrode 22 and the phosphor layer 23 on the glass substrate 21. Here, wiring is performed for each portion as shown in Fig. 8. By this wiring, the electrode layer 52 is grounded, and a negative voltage is applied from the power source 31 to the electrode layer 54. Furthermore, the inter-cathode and anode voltage is applied between the electron emission device 50 and the opposite substrate 20 by the power source 32. However in the state shown in Fig. 8, the switch 33 is opened, so that no voltage is applied. When a voltage is applied to both sides of the electron emission layer 55 by the electrode layers 52 and 54, election emission as shown by the arrow in the figure occurs in the surface portion of the electron emission layer 55.

[0035] When the switch 33 is closed and the inter-cathode and anode voltage is applied, electrons emitted on the surface of the electron emission layer 55 fly toward the opposite substrate 20 on the anode side. By collision of the electrons traveling from the cathode to the anode, the phosphor layer 23 emits fluorescence. Here, for convenience of explanations, only the constituent components for one pixel are shown. If the constituent components of one pixel are arranged in a matrix fashion vertically and horizontally, the flat display panel in which pixels are arranged on a two-

dimensional plane can be realized. Note that in such flat display panel, the switch 33 is kept close, and by adjusting the application voltage from the power source 31 for each pixel, the light emission state for each pixel is generally controlled. To be more specific, by adjusting the value of the application voltage given to the electron emission layer 55 and the application time, a quantity of flying of the electrons toward the opposite substrate 20 can be controlled.

[0036] In the structure shown in Fig. 10, a step difference is provided in the structure shown in Fig. 7. Specifically, as shown in Fig. 10(a), the three-layered structural body in which the lower electrode layer 62, the middle insulative layer 63 and the upper electrode layer 64 are laminated is formed on the supporting substrate 61 (not shown). In this three-layered structural body, the side portion adopts a step difference structure. Accordingly, the electron emission layer 65 is formed in this step difference structure portion as shown in Fig. 10(b). Here, the electron emission layer 65 is a layer obtained by dispersing electrically conductive fine particles in a high resistance layer, similarly to the example shown in Fig. 5. Also with such structure, the electron emission layer 60 can be formed.

[0037] In brief, a feature of the present invention is the particular method to form the electron emission layer by dispersing the fine particles formed of the electrically conductive material in the high resistance layer formed of the electrically insulative material, and the electron emission device may be constituted in the manner that the pair of electrode is allowed to contact, in any style, the electron emission device formed by this method.

[0038] <u>§ 4. Basic principle of the manufacturing method of the electron emission device according to the present invention</u>

A basic concept of the present invention has reference to the point that a resin layer showing thermal plasticity is formed on a substrate, fine particles formed of an electrically conductive material are implanted from the surface of the resin layer in a state where the resin layer is softened by heating this resin layer, and thus an electron emission layer in which the fine particles are dispersed at

positions located at a predetermined depth from the surface of the resin layer is formed. This method will be described with reference to the side section flow diagrams of Fig. 11 hereinafter.
[0039] As shown in Fig. 11(a), the supporting substrate 11 for forming the electron emission device is first prepared. As this supporting substrate 11, an electrically insulative substrate like a glass substrate may be employed, or the supporting substrate 11 may be the one in which an electrically insulative film is formed on an electrically conductive substrate such as a metal substrate. Subsequently, as shown in Fig. 11(b), the pair of electrodes 12 and 13 is formed on this supporting substrate 11. Plan shapes of these electrodes 12 and 13 on the substrate are illustrated in the plan view of Fig. 2. As a material of the electrodes 12 and 13, any material may be employed as long as the electrodes 11 and 12 are formed of an electrically conductive material functioning as an electrode. Moreover, as a method to form the electrodes 12 and 13 having the plane shapes as shown in Fig. 2, any method may be used. For example, if a metal layer is deposited on the supporting substrate 11 by an evaporation method or a sputtering method and this metal layer is patterned by a general photolithography method, the electrodes 12 and 13 having the predetermined plan shapes can be formed. Alternatively, metal paste, that is, resin or the like including metal particles, is printed on the supporting substrate 11 with a predetermined pattern, and a baking step is performed for this printing layer, thus forming the electrode 12 and 13.
[0040] Note that in Fig. 11, for convenience of explanation, though a step for forming a single electron emission device on the supporting substrate 11 is shown, it is general that a large number of electron emission devices are practically formed on the supporting substrate 11. For example, if the electron emission device is used for a flat display panel, a large number of electron emission devices are arranged on the supporting substrate 11 in a matrix fashion, and one electron emission device must performs a display as one pixel. Accordingly, a plurality of section, each of which cor-

responds to corresponding one of pixels, are practically defined on this supporting substrate 11, and an independent electron emission device is formed for each pixel,respectively. In other words, the electron emission device 10 shown in Fig. 2 is one device formed in one section on the supporting substrate 11, and a large number of such devices are arranged on the supporting substrate 11 vertically and horizontally. The pair of electrodes 12 and 13 shown in Fig. 11(b) is an electrode formed in one section for constituting one electron emission device, and such pair of electrodes 12 and 13 is practically formed for each section on the supporting substrate 11, respectively.

[0041] Subsequently, a resin layer 15 is formed on the entire surface of this supporting substrate 11, as shown in Fig. 11(c). This resin layer 15 may be formed by use of a general resin coating method such as a spin coating method. This resin layer 15 is a layer which functions afterward as a medium layer serving as a constituent component of the electron emission layer, and also a layer formed of resin having electrical insulation performance and thermal plasticity. As described above, in Fig. 11, though only an area equivalent to one section on the supporting substrate 11 is shown, a large number of sections are practically defined on the supporting substrate 11, and the resin layer 15 formed on the entire surface of the supporting substrate 11 overpasses the plurality of sections. Here, the resin layer 15 formed so as to overpass the plurality of sections shall be called a wide area resin layer 15.

[0042] Next, patterning is performed for this wide area resin layer 15, and only a portion of a predetermined specific region defined for each section is left as a resin layer (high resistance layer) 14a. This specific region is a region occupied by the electron emission layer 14 shown by a rectangle in the plan view of Fig. 2, and corresponds to a plan region in which the individual electron emission layer 14 is finally to be formed. As the patterning method for the wide area resin layer 15, a general photography method may be employed. Finally, as shown in Fig. 11(e), an implanting treatment to implant the electrically conductive fine particles 14b from

the surface of the individual resin layer 14a patterned is performed. At this time, if the resin layer 14a is softened by heating the resin layer 14a, the electrically conductive fine particles 14b make progress from the surface of the resin layer inwardly, and are buried at predetermined deep positions. Thus, the electron emission device shown in Fig. 5 is obtained. Note that, as the method to implant the fine particles, a cluster evaporation method, a gas deposition method, a reactive gas deposition method or the like may be used. Concrete explanations for these methods will be described later.

[0043] Moreover, in the foregoing embodiments, as shown in Fig. 11(c), after the wide area resin layer 15 is formed by coating it on the entire surface of the supporting substrate 11, the wide area resin layer 15 is patterned, and thus the resin layer 14a is formed for each specific region. Alternately, a printing screen having a planar patterning corresponding to each specific region is prepared, and the resin layer 14a shown in Fig. 11 (d) may be directly formed from a state shown in Fig. 11(b) by a printing step.

[0044] As described above, the method according to the present invention, in which the resin layer having thermal plasticity is formed on the substrate, the fine particles formed of the electrically conductive material are implanted from the surface of the resin layer in a state where this resin layer is softened by heating the resin layer, and thus, the electron emission layer in which the fine particles are dispersed at the predetermined deep positions from the surface of the resin layer, exhibits a merit that the electron emission layer in which the fine particles are uniformly dispersed can be obtained comparatively easily. As the method to form the resin layer containing the fine particles, the method is generally adopted, in which resin containing the electrically conductive fine particles is previously prepared, this resin is coated on the substrate, and thereafter this resin is cured by drying the resin. However, with such method, aggregation of the fine particles occurs in curing the resin, so that it is difficult to form a resin layer in which the fine particles are uniformly dispersed. Accord-

ing to the method of the present invention, because the technique to implant the fine particles from the surface of the resin layer after the formation of the resin layer is adopted, it is possible to disperse the fine particles uniformly all over the entire surface of the resin layer.

[0045] <u>§ 5. An implantation method of the fine particles</u>

Here, a concrete method for implanting the electrically conductive fine particles to the resin layer will be exemplified based on the embodiment illustrated.

[0046] (1) Cluster evaporation method

First, the chamber 80 as shown in Fig. 12 is prepared. In the chamber 80, the crucible 81 is prepared and the electrically conductive material 82 is enclosed in this crucible 81. The crucible 81 is heated by the heater 83, and the heated electrically conductive material 82 is evaporated in the chamber 80. On the other hand, the substrate holder 84 and the heater 85 for heating the substrate holder 84 are placed on the upper portion of the chamber 80, and the supporting substrate 11 is held by the substrate holder 84. Moreover, the shielding mask 86 is attached below the supporting substrate 11. In this shielding mask 86, an opening window having a predetermined shape pattern is formed. Air in the chamber 80 is exhausted from the air exhaustion pipe 87 by a vacuum pump (not shown), and the chamber 80 is kept in a predetermined vacuum.

[0047] In such system, when the crucible 81 is heated by the heater 83 while keeping the chamber 80 at a predetermined vacuum by exhausting air from the chamber 80, and the electrically conductive material 82 is evaporated, the evaporated ellectrically conductive material form fine particles in the chamber 80. Accordingly, as shown in Fig. 11(d), the supporting substrate 11 in which the resin layer 14a is formed on its upper surface is attached below the substrate holder 84 so as to be turned upside down (though such situation is not illustrated in Fig. 12, the resin layer 14a is formed on the lower plane of the figure of the supporting substrate 11), and the substrate 84 is heated by the heater 85. The resin

layer 14a on the supporting substrate 11 is softened previously. Accordingly, the fine particles formed of the electrically conductive material are implanted from the surface of this resin layer 14a (lower plane of the supporting substrate 11 in Fig. 11). At this time, existence of the shielding mask 86 allows only the fine particles which passed through the opening window of the shielding mask 86 to be implanted to the resin layer 14a. Specifically, it is possible to selectively implant the fine particles to a region corresponding to the opening window of the shielding mask 86.

[0048] The sizes of the fine particles implanted and the depth to which the fine particles are implanted in the resin layer 14a can be controlled by adjusting the vacuum in the chamber 80, the heating temperature of the crucible 81 and the heating temperature of the substrate holder 84. In this embodiment, the electrically conductive material 82 and the resin layer 14a are heated indirectly by the heaters 83 and 85, and the electrically conductive material 82 and the resin layer 14a may be directly heated by use of a laser beam or a xenon lamp.

[0049] (2) A gas deposition method

First, as shown in Fig. 13, two chambers are prepared. The first chamber 110 is a chamber for evaporating the electrically conductive material to generate the fine particles, and the second chamber 120 is a chamber to perform implantation of the fine particles by discharging the fine particles, which are generated in the first chamber 110, from the nozzle 121 to the surface of the resin layer 14a on the supporting substrate 11. The supporting substrate 11 is placed on the movement stage 122.

[0050] In the first chamber 110, the crucible 112 for housing the electrically conductive material 111 is provided, and this crucible 112 is heated by a heating apparatus (not shown). Helium as inert gas is introduced into the chamber 110 by the gas introduction pipe 113. The first and second chambers 110 and 120 are communicated by the movement pipe 114, and air in the second chamber 120 is exhausted by a vacuum pump (not shown) via the exhaustion pipe 123. Therefore, a gas flow path from the first chamber

110 to the second chamber 120 via the movement pipe 114 is formed, and air in the first chamber 110 is transferred into the second chamber 120 based on pressure difference between the first and second chambers 110 and 120. Thus, air is exhausted from the nozzle 121.

[0051] The air exhaustion from the exhaustion pipe 123 is performed while introducing helium gas from the gas introduction pipe 113, and the first and second chambers 110 and 120 are kept at each predetermined vacuum, respectively. In such situation, when the electrically conductive material 111 is evaporated by heating the crucible 112, vapor of the electrically conductive material will be filled in the chamber 110. Then, in the chamber 110, atoms or molecules of the electrically conductive material dispersed are combined with each other, and the electrically conductive fine particles are generated. The fine particles are discharged from the nozzle 121 via the movement pipe 114.

[0052] On the movement stage 122, the supporting substrate 11 on which the resin layer 14a is formed is placed as shown in Fig. 11(d). Since the movement stage 122 is heated by heating means (not shown), the resin layer 14a on the supporting substrate 11 gets softened by heating. Accordingly, the fine particles discharged from the nozzle 121 are implanted to the inside of the resin layer 14a from its surface.

[0053] Fig. 14 is a perspective view showing the positional relation ment between the supporting substrate 11 placed on this on com- stage 122 and the nozzle 121. In this example, nine rting sub- posed of 3 rows and 3 columns are defined on the e resin layer strate 11, and the pair of electrodes 12 and 13 is a matter of 14a are formed for each section, respecti d for the flat dis- course, when the electron emission devi defined on the sup- play panel, more large number of s charged from the noz- porting substrate 11. The fine p supporting substrate 11. zle 121 are blown to an upper e the supporting substrate Here, the movement stage owing direction of the nozzle 11 freely on a plane ver

121. Specifically, the supporting substrate 11 can be moved in the direction indicated by the arrow X and the arrow Y in Fig. 14. After all, it is possible to scan the position of the nozzle 121 for the substrate plate of the supporting substrate 11. Moreover, an open-close valve is provided inside the nozzle 121, and it is possible to control the discharge/non-discharge of the fine particles by this open-close valve. Accordingly, by controlling the open-close operation of the nozzle 121 and the movement operation by the movement stage 122, it is possible to implant the fine particles only to an optional region on the supporting substrate 11. To be concrete, in Fig. 14, if the fine particles are allowed to be discharged from the nozzle 121 and to be implanted only when the nozzle 121 is scanning each specific area in which the resin layer 14a is formed, the fine particles can be selectively implanted to a desired region.

[0054] The sizes of the fine particles implanted and the depth to which the fine particles are implanted in the resin layer 14a can be controlled by adjusting the heating temperature of the crucible 112, the heating temperature of the movement stage 122., pressure in both chambers, and a diameter of the ejection port of the nozzle 121. After all, various kinds of parameters may be adjusted so that the fine particles are discharged from the nozzle 121 at a speed suitable for the implantation. Moreover, in this embodiment, though the electrically conductive material 111 and the resin layer 14a are indirectly heated by heating means (not shown), the electrically conductive material 111 and the resin layer 14a may be directly heated by use of a laser beam and a xenon lamp.

[0055] (3) Reactive gas deposition method

In the gas deposition method shown in Fig. 13, helium gas as inert gas was introduced into the first chamber 110. When the electrically conductive material 111 is heated to be evaporated while introducing reactive gas having a nature to generate an electrically insulative compound by reacting with the electrically conductive material into the first chamber 110 together with inert gas, it is possible to generate fine particles formed of the electrically conductive material, the surface of which is covered with the electri-

cally insulative compound. For example, when aluminium is used as the electrically conductive material 111 and oxygen is introduced as the reactive gas, the fine particles formed of aluminium, the surface of which is covered with an oxide film (electrically insulative compound), can be generated. Then, in the second chamber 120, the electrically conductive fine particles, the surfaces of which are covered with the electrically insulative film, are implanted into the resin layer 14a.

[0056] Fig. 15 is a plan section view showing a state where such electrically conductive fine particles covered with the electrically insulative film are implanted into the resin layer 14a. As shown in the figure, the insulative film 14c is formed on the surface of the individual electrically conductive fine particle dispersed in the resin layer 14a. The advantage obtained by forming the electrically insulative film on the surface of the individual conductive fine particles is that these fine particles behave electrically as individual separate one even if adjacent fine particles physically contacting each other happen to exist as the fine particles P1 and P2 in Fig. 15 in the resin layer 14a. When the electrically insulative film is not formed on the surface of the fine particle, the fine particles P1 and P2 behave electrically as one fine particle, and the electron emission comes to occur not so often. Moreover in terms of the whole of the electron emission layer 14, the distribution of the fine particles is undesirably uneven. However, when the electrically insulative film is formed on the surface of the fine particle, the plurality of fine particles behave electrically as separate fine particles even if they contact with each other physically. Therefore, the above described problem does not occur. In such aspect, the reactive gas deposition method is more advantageous than the foregoing gas deposition method.

[0057] It is not necessarily required to form the electrically insulative film in the first chamber 110. For example, the reactive gas is introduced on the way of the transfer pipe 114, and the electrically insulative film may be formed on the surface of the electrically conductive fine particle during transferring the reactive gas in the

transfer pipe 114. Alternatively, the reactive gas is introduced in the vicinity of the ejection port of the nozzle 121 in the second chamber 120, and the electrically insulative film may be formed on the surface thereof, just before the implantation of the fine particle.

[0058] §6. Other embodiments

In the basic embodiments described above, as shown in Fig. 11(d), the independent resin layer 14a is formed in each specific area defined for each section. As shown in Fig. 11(e), the implantation of the fine particles is selectively performed only to each specific area of the whole area on the supporting substrate 11. Such selective implantation can be performed, like the embodiment shown in Fig. 12, in such manner that the shielding mask 86 having the opening window corresponding to the specific area of each section is disposed, and the fine particles are implanted through this opening window. Like the embodiment shown in Fig. 13, the implantation can be performed also by scanning the nozzle 121 while discharging the fine particles from the nozzle 121.

[0059] As against to such fundamental embodiments, it is possible to adopt an embodiment in which the fine particles are implanted to the entire surface of the wide area resin layer 15. Specifically, as shown in Fig. 11(c), the wide area resin layer 15 is formed on the whole region overpassing a plurality of sections on the supporting substrate 11, and, as shown in Fig. 16(a), the electrically conductive fine particles 14b are implanted to the whole region of the wide area resin layer 15. Then, the wide area resin layer 15 for which this implantation was performed is subjected to patterning to leave only the individual specific area defined for each section. As shown in Fig. 16(b), the independent resin layer 14a is formed in each specific area, respectively. Thus, the electron emission device having the structure similar to that of the foregoing fundamental embodiment is obtained.

[0060] Alternatively, as shown in Fig. 16(c), it is also possible to

implant the fine particles selectively only to the individual specific area defined for each section, among the whole region of the wide area resin layer 15. For this selective implantation, the shielding mask may be used or the nozzle scanning may be performed as mentioned above. When the selective implantation to such wide area resin layer 15 is performed, regions where the electrically conductive fine particles 14b are dispersed are the specific area defined for each section as shown in Fig. 16(c), in spite of the formation of the wide area resin layer 15 itself on the whole of the substrate. Since the region where the electrically conductive fine particles 14b were not implanted function merely as an electrically insulative film, each electron emission device can function as an independent device even in the state shown in Fig. 16(c), without the special need of the patterning for the wide area resin layer 15 being darely performed. However, in actual manufacturing processes, various kinds of impurities may be gotten mixed in the wide area resin layer 15, and a current leak may be caused between the adjacent devices by the impurities. Thus, it is favorable that the patterning is practically performed further for the wide area resin layer 15, from the state shown in Fig. 16(c), so as to leave only the specific area defined for each section and finally, the structure shown in Fig. 16(b) is obtained.

[0061] Note that if this wide area resin layer 15 is formed by use of resin offering photosensitivity, patterning can be performed for the photosensitive wide area resin layer 15 by a direct exposure. Accordingly, a resist layer for the patterning needs not to be newly formed, and the manufacturing processes are simplified.

[0062] Although the conventional forming treatment is not always necessary for the electron emission layer manufactured by the method according to the present invention, an electron emission characteristic can be improved by performing the forming treatment. Specific, as shown in Fig. 11(e), after the implantation of the electrically conductive fine particles 14b is completed, current is made to flow between both electrodes 12 and 13, and properties of the resin layer 14a can be changed by Joule heat generated by

this energizing. The resin layer 14a is the one functioning as a high resistance layer in the electron emission layer 14, and if the properties of the resin layer 14a are changed under predetermined conditions, the electron emission characteristic can be improved.

[0063] Moreover, if the resin layer 14a is formed by use of resin having an electrical polarity, the pauling treatment can be performed after the impantation of the electrically conductive fine particles 14b. Specifically, the resin layer 14a is softened by heating while applying electrical field in a predetermined direction to the structural body shown in Fig. 11(e). Upon application of the electrical field, each molecule of the resin is oriented in a direction in accordance with the electrical field, and the dispersed electrically conductive fine particles 14b offer a certain orientation. If the resin layer 14a is made to be polymerized by cooling it slowly while keeping the orientation, the electron emission layer 14 finally obtained becomes a layer offering a predetermined orientation. Specifically, the orientation in terms of a shape of the dispersed electrically conductive fine particle 14b or the orientation relating to an atomic spin becomes even in the electron emission layer 14, and more stable electron emission can be expected.

[0064] It is satisfactory that the implantation operation of the fine particles in the case of manufacturing the planar type electron emission device shown in Figs. 1 to 5 is performed so as to implant the fine particles to a direction perpendicular to the substrate plane. In the case where so called a vertical type electron emission device shown in Figs. 7 to 10 is manufactured, effective implanting directions need to be taken into account, respectively. For example, to form the electron emission layer 55 in the structure shown in Fig. 7(b), it is most effective to implant the fine particles from the direction in parallel with the substrate plate approximately, that is, the direction perpendicular to the surface of the layer 55. However, since it is practically difficult to implant from such direction, the structure shown in Fig. 10(b) should be adopted, so that the implantation obliquely from the above is made to be possible.

[0065] As a concrete technique to perform the implantation obliquely from the above, a technique of an oblique evaporation in which a substrate is disposed so as to be slanted to an evaporation source in a chamber should be adopted in the case of a cluster evaporation method. Moreover, in the case of a gas deposition method, a nozzle should be disposed so that fine particles are discharged to a substrate obliquely from the above with an angle relative to the substrate.

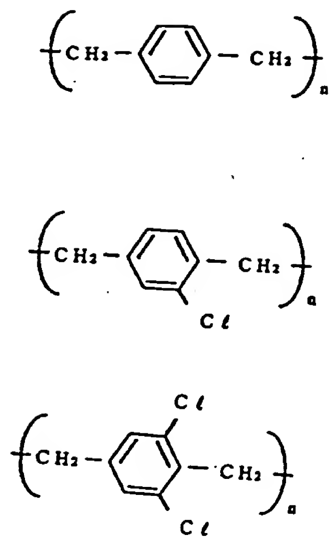
[0066] § 7. Electrically conductive material and resin material

The electrically conductive material used in embodying the present invention, that is, the material used for the dispersed fine particles, may be any material as long as it is an electrical conductive material. That is to say, in addition to metals such as gold, silver, copper and aluminium, metal compounds such as SnO_2, In_2O_3 and PbO and semiconductors such as carbon can be used.

[0067] On the other hand, the resin material functioning as a dispersing medium for this fine particles may be a material having a thermal plasticity(the resin material should be softened at a temperature as low as possible) and electrically insulation properties. In general, to function as a high resistance layer for the electrically conductive fine particles, it is said that the resin layer should have an insulative property of a specific resistiviy of 10^{14} $\Omega \cdot$cm or more. To be concrete, polyethylene, vinyl chloride resin, polypropylene, styrene resin, ABS resin, polyvinyl alcohol, acrylic resin, acrylonitrile-styrene resin, vinylidene chloride resin, AAS(ASA) resin, AES resin, cellurose derivative resin, thermoplastic polyurethane, polyvinyl butyral, poly-4-methyl pentene-1, polybutene-1 and rosin ester can be used. The following resins are especially desirable with respect to heat resistance and humidity resistance: fluoresin , for example, polytetrafluoroethylene, fluorinated ethylene propylene, tetra fluoroethylene-perfluoroalkylvinylether copolymer, or their dispersion type or modified type (coating type) , or polypara-xylene expressed by the following structure formulae.

[0068]

[Chemical 1]



N-type

C-type

D-type

Note that the C-type may be resin in which one portion other than the main chain bonding portion in benzene ring is substituted by chloride in addition to the above described resins, and the D-type may be resin in which two portions other than the main chain bonding portion in benzene ring are substituted by chloride in addition to the above described resins.

[0069]

[Example] Examples of the present invention will be described below.

[0070] (1) First example

Solution obtained by dissolving 10 g of rosin ester resin (trade name: Steberite ester 10) as thermal plastic resin in 50 g of tetrahydro furan as solvent was prepared. Then, this solution was spinner-coated on the glass substrate 11 in which a predetermined electrode layer was formed at a speed of 1000 rpm for 90 sec, and then left to stand at 60 ℃ and for one hour to dry the solvent. Thus, a rosin ester layer having a uniform thickness of 2 μm was formed on the entire surface of the substrate.

[0071] Subsequently, the above described glass substrate 11 was fitted to the substrate holder 84 in the chamber 80 shown in Fig. 12, in a state where the bottom surface of the glass substrate 11

was made to contact with the substrate holder 84. On the other hand, the pellet formed of copper (Cu) as the electrically conductive material82 was introduced into the crucible 81. Then, air exhaustion was performed while introducing nitrogen gas into the chamber 80, and the inside of the chamber 80 was kept at pressure of about 10 Pa. Here, the crucible 81 was heated, and the copper was evaporated. As a result, the fine particles formed of copper were implanted into a region corresponding to the opening window of the shielding mask 86 in the resin layer softened on the substrate 11. The structure was obtained, in which the copper fine particles were dispersed in the rosin ester layer. The state was confirmed, in which an average diameter of the copper fine particles was about 20 nm, and the copper fine particles were dispersed uniformly in a depth of about 40 nm from the surface of the resin layer. When a voltage was applied to the electron emission layer obtained in the above described manner, a good electron emission from the surface thereof was recognized.

[0072] (2) Second example

As shown in Fig. 13, the two chambers were prepared. Aluminium as the electrically conductive material 11 was housed in the crucible 112 in the first chamber 110. On the other hand, the substrate 11 in which the rosin ester resin layer of a thickness of about 2 μm was formed like the first example was housed in the second chamber 120. Air was exhausted from the exhaustion pipe 123 while introducing helium gas as inert gas into the first chamber 110. Thus, pressure in the first chamber 110 was kept at about 5×10^4 Pa, and pressure in the second chamber 120 was kept at about 5×10^2 Pa. In such situation, the crucible 112 was heated, and aluminium was evaporated. As a result, the alminium fine particles discharged from the nozzle 121 were implanted into the resin layer softened on the substrate 11, and the structure in which aluminium fine particles were dispersed into the rosin ester resin layer was obtained. The state was confirmed, in which an average diameter of the aluminium fine particles was about 20 nm, and the aluminium fine particles were dispersed uniformly in a depth of

about 40 nm from the surface of the resin layer. When a voltage was applied to the electron emission layer obtained in the above described manner, a good electron emission from the surface thereof was recognized.

[0073]

[Effects of the Invention] According to the present invention as described above, in the state where the resin layer having thermal plasticity was softened by heating, the fine particles formed of the electrically conductive material are implanted from the surface thereof. Accordingly, the electron emission device capable of stably emitting electrons can be manufactured with simple processes.

[Brief Description of the Drawings]

[Figure 1] Fig. 1 is a section view showing a structure of a general surface conduction type electron emission device 10 conventionally proposed and an opposite substrate 20.

[Figure 2] Fig. 2 is a top surface view of a constituent component formed on a glass substrate 11 in the electron emission device 10 shown in Fig. 11, and a section taken along the line I-I in Fig. 2 is shown in Fig. 1.

[Figure 3] Fig. 3 is a section view showing a state where electrons are being emitted from the electron emission device 10 shown in Fig. 1.

[Figure 4] Fig. 4 is a section view showing a method to form an electron emission layer 14 of the electron emission device 10 shown in Fig. 1 by a forming treatment.

[Figure 5] Fig. 5 is an enlarged section view for explaining a basic constitution of an electron emission layer in an electron emission device, which was manufactured by a manufacturing method according to the present invention.

[Figure 6] Fig. 6 is a diagram showing a distribution state of particles in the electron emission layer shown in Fig. 5.

[Figure 7] Fig. 7 is a perspective view showing a concrete structure of the electron emission device 50 according to another embodiment to which the manufacturing method according to the pre-

present invention is applied.

[Figure 8] Fig. 8 is a section view showing a structure of the electron emission device 50 and the opposite substrate 20 shown in Fig. 7.

[Figure 9] Fig, 9 is a section view showing a state where electrons are being emitted from the electron emission device 50 shown in Fig. 7.

[Figure 10] Fig. 10 is a perspective view showing a concrete structure of the electron emission device 60 according to still another embodiment to which the manufacturing method of the present invention is applied.

[Figure 11] Fig. 11 is a side section manufacturing step showing a basic manufacturing method of the electron emission device according to the present invention.

[Figure 12] Fig. 12 is a conception view showing an example of an implantation method of electrically conductive fine particles in the present invention.

[Figure 13] Fig. 13 is a conception view showing another example of an implantation method of electrically conductive fine particles in the present invention.

[Figure 14] Fig. 14 is a perspective view showing a detailed structure in a second chamber 120 in Fig. 13.

[Figure 15] Fig. 15 is a plan sectional view showing a state where fine particles are dispersed, each having an electrically insulative film formed on its surface.

[Figure 16] Fig. 16 is a step diagram showing a manufacturing method according to another embodiment of the electron emission device according to the present invention.

[Explanations of Reference Numerals]

10.....electron emission device, 11......supporting substrate (glass substrate), 12......electrode, 13......electrode, 14......electron emission layer, 14a......resin layer (high resistance layer), 14b......electrically conductive fine particles, 14c......electrically insulative film, 14Z....electrically conductive thin film, 15.....wide area resin layer, 20.....opposite substrate, 21.....glass substrate,

22.....transparent electrode, 23....phosphor layer, 31....power source, 32....power source, 33.....switch, 34.....power source, 41.....electrically conductive fine particle, 42......high resistance layer, 50......electron emission device, 51.....supporting substrate, 52.......lower electrode layer, 53.....middle electrically insulative layer, 54.....upper electrode layer, 55......electron emission layer, 60.....electron emission device, 61......supporting substrate, 62.....lower electrode layer, 63.......middle electrically insulative layer, 64.....upper electrode layer, 65......electron emission layer, 80.....chamber, 81.....crucible, 82......electrically conductive material, 83.....heater, 84......substrate holder, 85......heater, 86......shielding mask, 87......exhaustion pipe, 110......first chamber, 111......electrically conductive material, 112.......crucible, 113.......gas introduction pipe, 114......transfer pipe, 120......second chamber, 121......nozzle, 122......movement stage, 123.....exhaustion pipe, D1......diameter of electrically conductive fine particle, D2....distance between electrically conductive fine particles, I1......diode current, I2.......emission current, If........current for forming, P1 and P2......fine particle, V1.....application voltage, V2......anode voltage.

Fig. 1

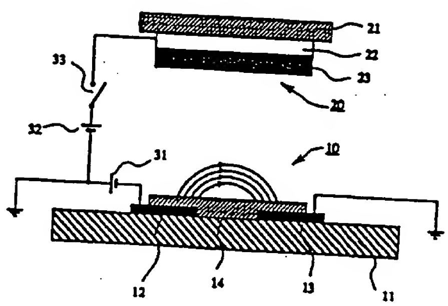


Fig. 2

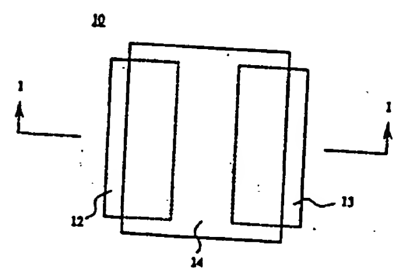


Fig. 3

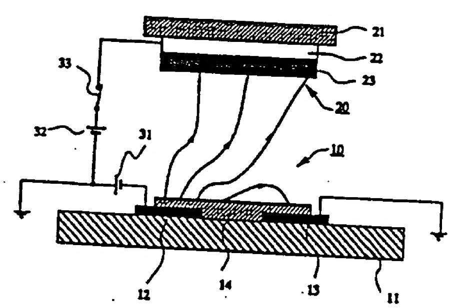


Fig. 4

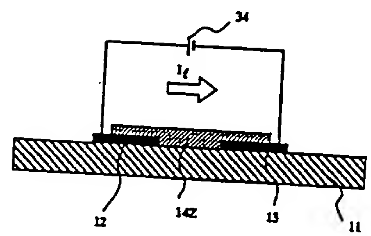


Fig. 5

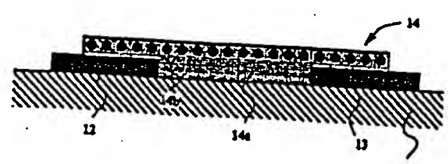


Fig. 6

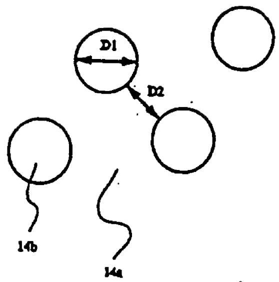


Fig. 7

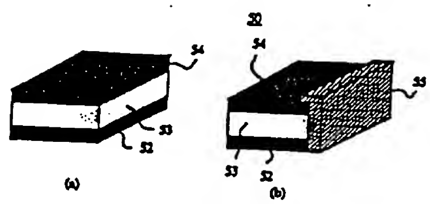


Fig. 8

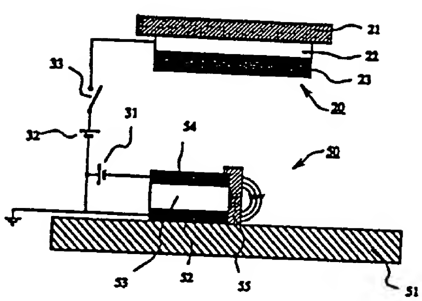


Fig. 9

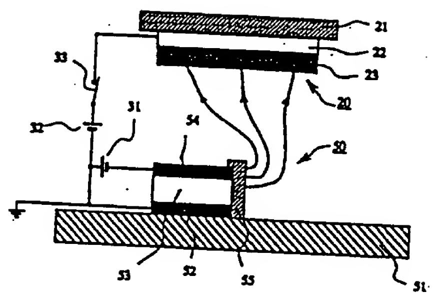


Fig. 10

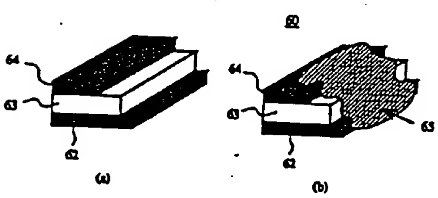


Fig. 12

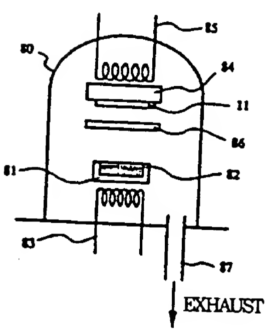


Fig. 13

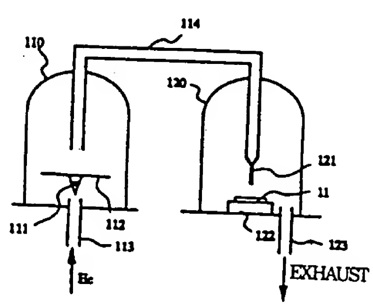


Fig. 11

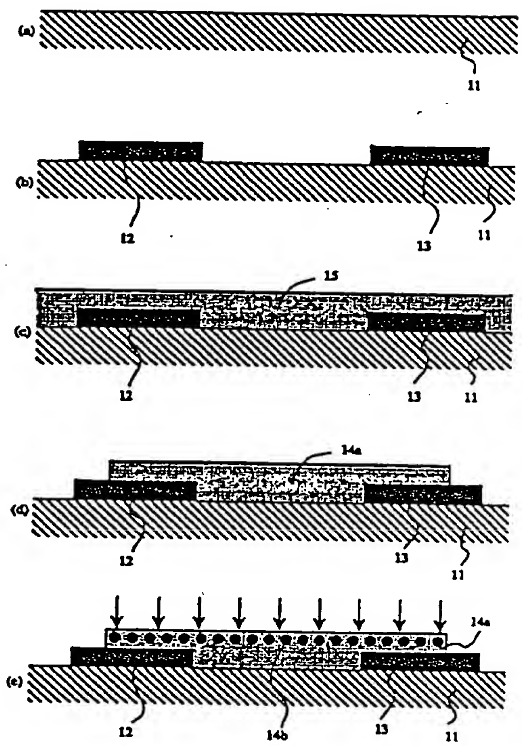


Fig. 14

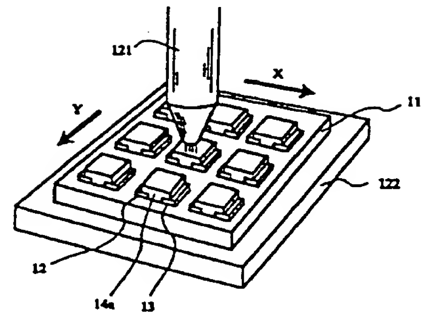


Fig. 15

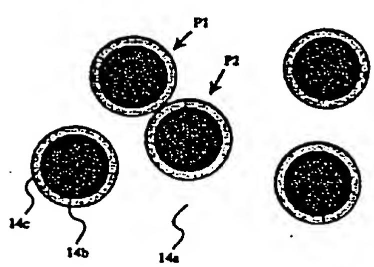


Fig. 16